**ABSTRACT**

**Title of Thesis: "HAPSITE® Gas Chromatography - Mass Spectrometry with Solid Phase Microextraction"**

Author: CAPT Waikwong Kan
Master of Science in Public Health

Thesis Directed by: CDR Gary L. Hook
Assistant Professor
Department of Preventive Medicine and Biometrics

Rapid air sampling can be accomplished with solid phase microextraction (SPME) to avoid the difficulties of pumps and wet chemistry. Gas chromatography with mass spectrometry (GC/MS) is the gold standard for identifying volatile and semi-volatile chemicals. Combining SPME with a portable HAPSITE GC/MS may allow rapid chemical identification outside of a laboratory. Six chemicals at six concentrations were tested using four sample introduction methods. The four methods included the HAPSITE loop, the HAPSITE with tri-bed concentrator, the HAPSITE with SPME and a field portable GC/MS with SPME. The SPME fiber used was Polydimethylsiloxane (PDMS). The HAPSITE with tri-bed concentrator achieved the lowest detection limits. The HAPSITE and the field portable GC/MS instrument coupled with SPME had similar variability. The relative standard deviation for these instruments was under 25% for most chemicals with concentrations between 1-10 ppm.

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HAPSITE® Gas Chromatography - Mass Spectrometry with Solid Phase Micro Extraction

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**HAPSITE® GAS CHROMATOGRAPHY - MASS SPECTROMETRY**

**WITH SOLID PHASE MICROEXTRACTION**

BY

CAPT WAIKWONG KAN

Thesis submitted to the faculty of the Department of Preventive Medicine and Biometrics Graduate Program of the Uniformed Services University of the Health Sciences in partial fulfillment of the requirement for the Degree of Master of Science in Public Health, 2005

# DEDICATION

To my parents, thank you for bringing me into this world and for teaching me the importance of perseverance, a vital ingredient to success in any endeavor.

To my mentors, who guided me through challenges of life, I dedicate this thesis to you all.

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# CHAPTER ONE: INTRODUCTION

## Statement of the Problem

The demand for on-site analysis of field contaminants and the need for rapid results have been well documented [1-8]. High quality analytical data obtained in the field can result in savings of both time and money. More importantly, it is vital that the identity of unknown chemicals be rapidly determined when emergency response and military personnel are responding to hazardous material incidents or acts of terrorism. High quality data available on-site will help ensure first responders are adequately protected and improve consequence management efforts designed to minimize the negative effects of the event on people and the environment.

In addition to emergency response scenarios, there are military directives that drive the requirement for rapid field sampling and analysis that confirms the identity of unknown chemicals and allows the exposure assessment process to begin immediately. The force health protection requirements can be best accomplished by on-site analysis of unknown chemical exposures. Presidential Review Directive 5 requires the performance of operational exposure assessments whenever military troops are deployed [9].

Traditional sample preparation methods do not easily support rapid analysis in the field. Traditional sampling methods include trapping of analytes on a sorbent media during active air sampling or taking bulk air samples with tedlar bags or summa canisters. Bulk samples of soil or water may also be needed for analysis in a laboratory. Analytical instruments for the analysis of these samples often require wet chemistry preparation methods that are difficult to perform in field conditions. If the analysis cannot be

performed in the field, during a military deployment, shipment to an analytical laboratory in Europe or the United States can delay the results for weeks. Field portable analytical equipment capable of providing laboratory quality data will eliminate much of this delay.

The HAPSITE is a ruggedized Gas Chromatograph/Mass Spectrometry (GC/MS) used by the military and emergency responders to identify unknown chemicals. The system can be used to identify chemical warfare agents (CWA) and toxic industrial chemicals (TIC) to provide on-scene commanders with valuable data, enabling them to rapidly make informed decisions. This will ultimately help protect human health [11]. Solid Phase Microextraction (SPME), a solvent-free sample collection technique, coupled with field portable GC/MS has the potential to provide reliable and timely data in the field.

*SPME and HAPSITE GC-MS*

SPME extracts and concentrates organic chemicals onto a thin fused silica fiber coated with a polymeric phase [12]. The theory behind SPME is well described in Solid Phase Microextraction by Pawliszyn [13]. The SPME sampling device, shown in Figure 1-1, consists of a syringe barrel, plunger, syringe needle, and a coated fused silica fiber. The SPME extraction technique is a 2-step process: 1) analytes partition from the air or aqueous sample to the fiber coating, 2) the concentrated analytes partition off the fiber coating in the analytical instrument [14].

**Figure 1-1**: SPME fiber sampler

By exposing the SPME fiber to a liquid or the air, volatile and semi-volatile chemicals partition to the fiber. The fiber is then retracted into the syringe barrel and capped to reduce sample loss and protect the fiber. The SPME fiber is then inserted into a GC/MS through an injection port where the chemicals are thermally desorbed.

Compared to traditional sampling methods, SPME sampling often reduces sampling time and makes it possible to extract and concentrate chemicals from multiple environmental matrices. SPME has been shown to provide reliable data in the parts per billion (ppb) range [13]. Because of its portability and simplicity of operation, SPME provides flexibility in sampling multiple locations and matrices. After thermal desorption in the GC/MS, the SPME fiber is immediately ready to obtain additional samples.

GC/MS is the gold standard for identifying unknown volatile and semi-volatile chemicals. The GC portion of the system is typically a 30 meter capillary column that separates individual chemicals in a complex mixture. The separation of the component chemicals allows for both qualitative and quantitative analysis [15]. As the individual chemical components are released from the GC column, they enter the MS. In the MS, each chemical is ionized and passed through a magnetic mass analyzer that measures the amount of each ion present. The retention time of a chemical in the CG and the mass spectra provided by the MS allows for unambiguous identification of unknown chemicals. Coupling SPME sampling with field GC/MS analysis eliminates much of the time and cost associated with traditional field sampling and shipment for laboratory analysis [8].

Currently there are six types of fiber coatings commercially available. These fiber coating types and their recommended use are summarized in the Table 1-1. SPME sampling can be performed in three basic modes: direct extraction, headspace extraction and extraction with membrane protection. In the direct extraction mode, the fiber is inserted directly into the air or an aqueous sample and the analytes are extracted into the

**Table 1-1**: Types of SPME fiber coatings and their recommended use [16]

| Stationary Phase | Recommended Use |
|---|---|
| Polydimethylsiloxane (PDMS) | |
| 100um/non bonded* | Volatiles |
| 30 um/non bonded | Nonpolar semi volatiles |
| 7 um/bonded** | Nonpolar to moderately polar, semi volatiles |
| Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) | |
| 65um/partially crosslinked*** | Polar volatiles |
| 60um/ partially crosslinked | General purpose (for HPLC only) |
| Polydimethylsiloxane/Carboxen (PDMS/Carboxen) | |
| 75um/partially crosslinked | Trace-level volatiles |
| Carbowax/Divinylbenzene(CW/DVB) | |
| 65 um/partially crosslinked | Polar analytes |
| Carbowax/Templated Resin(CW/TPR) | |
| 50 um/partially crosslinked | Surfactants (for HPLC only) |
| Polyacrylate (PA) | |
| 85um/partially crosslinked | Polar semivolatiles |

Numbers indicate coating thickness

*Non-bonded phases are stable with some water-miscible organic solvents, but slight swelling may occur.

**Bonded phases are stable with all organic solvents. Slight swelling may occur when used with non-polar solvents.

***Partially crosslinked phases are stable in most water-miscible organic solvents. They may be stable in some non-polar solvents, but slight swelling may occur [16].

fiber coating. In the headspace mode, analytes are extracted from the pocket of air (headspace) above an aqueous sample. Headspace SPME sampling prevents potential fiber contamination from non-volatile, high molecular weight compounds in an aqueous sample. In membrane-protected SPME sampling, a selective membrane is used to separate the fiber from the sample. The membrane provides a means to filter out high molecular weight compounds that may contaminate the fiber [12].

Immediately after the fiber is exposed to the air or aqueous sample matrix, it is ready to be analyzed by a GC/MS. There are many brands of GC/MS instruments for use in laboratories; however, few field/man portable instruments are available. The Hazardous Air Pollution on Site (HAPSITE) manufactured by Inficon is a man portable GC/MS instrument and was selected for this research project. HAPSITE is designed for on-site chemical detection and identification of volatile organic chemicals (VOCs). It is a unique instrument capable of direct air sampling using only battery power. Its design enables the instrument to be taken into contaminated environments and through the requisite decontamination process. Because of its portability, the military services selected the HAPSITE as a primary tool for chemical agent identification, emergency response and general force health protection [10]. Currently, all samples must be in the vapor phase in order to enter the HAPSITE sampling probe. In order to expand the capabilities of the HAPSITE, the manufacturer installed a prototype SPME injection port.

The HAPSITE SPME injection system uses a Jade inlet. A cross sectional picture of the Jade inlet is shown in Figure 1-2. The inlet has a ball-and-seat valve that allows the SPME sampler to be inserted into the port through the needle guide. After pushing through the ball-and-seat valve, the actual fiber can be exposed and thermally desorbed in

the injection port. Once the SPME fiber is retracted and pulled out of the valve, the ball is pulled up by the ball magnet to seal off the opening in the injection port. This design is more durable than a septum because the septum requires frequent replacement [17].

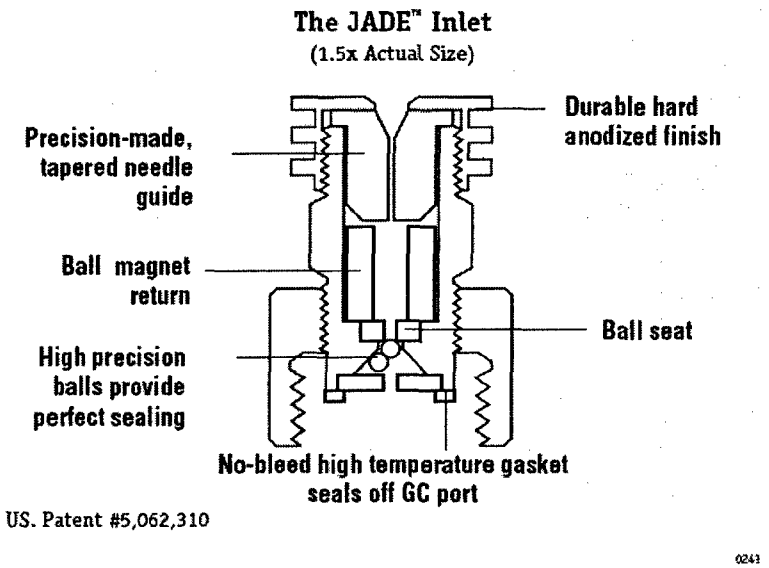



**Figure 1-2**: Cross sectional view of HAPSITE SPME injection port [17]

## Research Goal

The goal of this research was to determine whether SPME sample introduction could be incorporated into the HAPSITE and provide valid and reliable results. This was accomplished by evaluating the prototype HAPSITE SPME injection port system using six chemicals of various molecular weights that cover the operating range of the HAPSITE. Chromatographs of these chemicals generated with original HAPSITE sample inlet system (loop) and the new SPME injection port will be compared. These chemicals were also used to estimate the lower limit of detection and the reproducibility of the HAPSITE SPME system.

## Research Question

Can a SPME injection port be incorporated into the HAPSITE and provide reliable sample results with volatile chemicals?

**Specific Aim 1:**

Identify six TICs, ranging from a molecular weight of 45 atomic mass unit (AMU) to 300 AMU, with a boiling point less than 572 °F (300 °C), which represent the operating range of the HAPSITE [18]. Select a fiber coating and develop a SPME sampling method for the selected chemicals.

**Specific Aim 2:**

Estimate the lower limit of detection (LOD) and examine linearity across a range of concentrations for the six selected chemicals using the following sample introduction methods:

- Standard HAPSITE loop
- HAPSITE tri-bed concentrator
- HAPSITE SPME
- A field portable instrument with SPME

**Specific Aim 3:**

Compare the quality of the chromatography achieved with the standard HAPSITE loop, HAPSITE SPME, and the field portable instrument with SPME.

**Specific Aim 4:**

Compare the reproducibility of the data obtained using the four different sample introduction methods listed in Specific Aim 2.

## CHAPTER TWO: LITERATURE REVIEW

Field sampling with SPME followed by laboratory GC/MS analysis is well documented. However, little has been published regarding the use of SPME with a man portable GC/MS system. Much of the original fieldwork was accomplished using SPME with a GC and a detector such as flame ionization detector (FID), electron capture detector (ECD), and nitrogen phosphorous detectors (NPD) [3,19,20,21]. These detectors only provide retention time and relative intensity information and are of limited usefulness when identifying unknown chemicals. The rest of this chapter will cover studies related to the HAPSITE or the use of SPME for field detection.

Hook *et al.* [8] examined the use of SPME coupled with GC/MS for on-site detection of the nerve agent, O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX). In this study, clothing material sealed in a glass vial was spiked with 1 ul of neat VX. Five commercially available SPME fiber types were evaluated in order to select the optimal fiber. Head space sample extractions were performed and analyzed using a laboratory grade Agilent 6890/573 GC/MS Agilent instrument. PDMS was determined to be the optimal fiber coating. It was found that sampling and analysis could be accomplished in less than 20 minutes with RSDs of the peak areas ranging from 0.2% to 14%.

Using SPME and field portable GC/MS, Smith *et al.* [7] conducted a similar experiment to detect CS riot control agent in air. CS canisters were used to generate the atmosphere for sampling. Air samples were collected using portable air sampling pumps (at a rate of 2 liter/min) with a 37-mm polyterafluoroethylene (PTFE) filter followed by a sorbent tube loaded with Tenax TA. CS was released outdoors and air samples were

collected for 5 minutes at a distance of 3-4 feet. A Hewlett Packard 6890 GC with 5973 mass selective detector was used to analyze the filter and Tenax tube samples. For SPME fiber samples, two CS canisters were ignited inside a 10,000 $ft^3$ structure. An 85 um PA SPME fiber was exposed to the CS plume for 5 minutes. Within 2 minutes of collection, the fibers were analyzed using the Viking Spectra Trak 572 GC/MS instrument. CS epoxide was detected in almost all Tenax tube collectors, but not in the SPME samples. Unlike laboratory analysis of air samples, a solvent was not used to extract chemicals from SPME samples. As a result, early eluting peaks such as toluene, o-chlorobenzene and benzonitrile were detected in the SPME samples and not in the laboratory sample [7].

The Department of Defense (DoD) and Environmental Protection Agency (EPA) have conducted several studies designed to evaluate the performance of the HAPSITE. In one study, the HAPSITE and its headspace module were used to analyze VOCs in 14 ground water samples in order to determine the appropriate placement of monitoring wells at the Monterey Peninsula Airport. The HAPSITE was used to characterize the horizontal extent of Trichloroethene (TCE) plume contamination. Two years after the TCE characterization, the HAPSITE was used again to characterize the vertical extent of TCE contamination [22].

Another study determined the instrument identification limits (IIL) for 3 CWAs. The IIL was defined as "the minimum compound concentration needed to produce a full scan spectrum with a mass spectral quality fit (similarity index) of 700 or greater using the full National Institute of Standards and Technology (NIST) mass spectral database [23]." Similarity index (SI) is a term used by Inficon to estimate the probability of correct identification from results of mass spectral library searches (perfect fit would have a SI of

1,000). The HAPSITE similarity index is equivalent to the forward match factor in the NIST library search algorithm [24,25]. The objective of the study was to determine:

1) the IIL for sarin (GB), soman (GD), mustard (HD), 1,2-dibromoethane, 1-octanethiol and trichloroacetyl chloride,

2) the reproducibility of the IILs with randomized run sequence,

3) the level of analyte that resulted in carryover and,

4) the effect of diesel fuel contamination on each agent's IIL

In this study, if the blank run immediately after the sample run had a SI above 400 for the analyte of interest in the Reconstructed Ion Chromatogram (RIC), carryover effect was considered to be present. It is interesting to note the following adjustments were made to optimize the results of the study:

1) The automatic release of internal standards (Bromopentafluorobenzene (BPFB) and 1,3,5-Tris-Trifluoromethylbenzene (TRIS)) by the system was turned off due to the interference they caused with the analytes of interest.

2) The filament delay in the inlet method was adjusted based on the compound and solvent being analyzed.

3) The factory installed methods were modified such that the column temperature ramping rate was raised from 36 °F/min to 54 °F/min in order to improve the chromatography .

Table 2-1 is a summary of the range and average values of the IILs for three CWAs tested in the survey mode using the loop and concentrator methods. The reproducibility of the IILs was inconclusive since none of the instruments could consistently detect all chemicals. [23]

**Table 2-1:** Range (average values) of IIL in $mg/m^3$

| Chemical Tested | Survey mode with Concentrator | Survey mode with Loop |
|---|---|---|
| GB | 0.04 – 0.2 (0.095) | 0.84 – 6.40 (1.97) |
| GD | 0.04 – 0.75 (0.242) | 0.6 – 11 (2.65) |
| HD | 0.02 – 0.07 (0.038) | 0.60 – 107 (>20.2) |

Phase II of the study was designed to determine the IIL for HD, GB and GD at temperatures ranging from -25 to 110 ° F and relative humidity (RH) extremes (0 to 100%). It was also designed to assess the effects of environmental changes on the operational capabilities of the instrument. This was done by observing changes in the IIL. The set up of Phase II was identical to Phase I of the study. The overall changes in IIL due to variation of temperature and relative humidity were noted to be insignificant. Table 2-2 illustrates the effects of various combinations of temperature and humidity on the IIL [26].

**Table 2-2** IIL in $mg/m^3$ for the loop introduction mode at various combinations of temperature and humidity.

| Temp (F) | RH (%) | HD | GB | GD |
|---|---|---|---|---|
| 77 | 25 | 0.04 | 0.08 | 0.04 |
| 77 | >90 | 0.02 | 0.01 | 0.02 |
| 110 | 25 | 0.02 | 0.04 | 0.04 |
| 35 | 0 | 0.15 | 0.01 | 1.20 |

In 1997, another field test involving the HAPSITE was conducted by the Environmental Technology Verification Branch of the EPA. The HAPSITE was used to measure chlorinated volatile organic compounds in groundwater at two contaminated sites: Savannah River, S. Carolina and McClellan Air Force Base (AFB), CA. The

primary target compounds were trichloroethylene and tetrachloroethylene for the Savannah River Site and trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane and trans-1,3-dichloropropene for McClellan AFB. The headspace sample introduction method was used for the study. Instrument precision and accuracy were determined from analyses of replicate samples from 16 multi-component standard mixtures of known composition. Four replicate samples from each of the 16 standard mixtures were used to measure the precision of the HAPSITE. The median value of the RSD for all compounds was 12%, with a $95^{th}$ percentile of 29%. The median value of absolute percent difference (difference between the HAPSITE result and the known chemical concentration) of the HAPSITE measurement was found to be 8% with a $95^{th}$ percentile of 27%. The HAPSITE was able to detect all groundwater contaminants identified by standard laboratories for both test sites. All contaminant concentrations were above 5 ug/l. From this study it was concluded that the HAPSITE could provide valid results for environmental site characterization [27].

Smith *et al.* [5] compared two different field GC/MS systems, the man-portable HAPSITE and the field-portable Viking. This work examined the ability of these instruments to sample and identify components in a mixture of four volatile chemical warfare agents: Sarin (GB); soman (GD); cyclohexylmethylphosphonofluoroidate (GF) and sulfur mustard (HD). Pure standards of the four CWA were injected into a tedlar bag to achieve an air concentration of 5 $mg/m^3$ for each agent. SPME fibers were exposed to the CWA mix in the bag for five minutes, and then transferred to the SPME injection port of the Viking for analysis. The same air was sampled and analyzed using a HAPSITE. The Tenax concentrator was used in this study to concentrate analytes in the air sample.

The HAPSITE drew the sample from the tedlar bag at a rate of 250 ml/min for 1 minute. Overall, the Viking produced peaks with better resolution than the those generated by the HAPSITE .

Since the HAPSITE with a SPME injection system is a prototype, there is currently no research literature on the combination. By combining the HAPSITE GC/MS with SPME techniques, the versatility of the HAPSITE can potentially enhanced.

# CHAPTER THREE: METHODS

**Specific Aim 1:**

Identify six TICs, ranging from a molecular weight of 45 AMU to 300 AMU, with a boiling point less than 572 °F, which represent the operating range of the HAPSITE [18]. Select a fiber and develop a SPME sampling method for the selected chemicals.

To accomplish Specific Aim 1, the following chemicals were selected for testing:

1. Acrylonitrile (53amu, boiling point , bp, = 171 °F)
2. Benzene (78 amu, bp = 176 °F )
3. Trichloromethane (119.4 amu, bp= 143°F )
4. 1,3,5-Trimethylbenzene (120 amu, bp = 329 °F )
5. O-Chlorotoluene (126 amu, bp = 323 °F )
6. Hexachlorobutadiene (mw = 260, bp = 419 °F ) [28].

Fiber Preparation

The following three SPME fiber coating types were tested: 100 um polydimethylsiloxane (PDMS), 85 um polyacrylate (PA) and 65 um PMDS/divinylbenzene (DVB). These fibers were purchased from Supelco (Bellefonte, PA). Before use, each fiber was conditioned according to the manufacturer's recommendations [29]. In addition, blank runs were completed each day before running any fiber samples.

Sample Preparation

In order to select for the optimal fiber, each fiber type was exposed to a standard mixture of 1 ppm for each test chemical. Pure standards were purchased from Sigma Aldrich (St. Louis, MO). To mix the 1 ppm air concentrations for each of the six test chemicals, individual chemical stock solutions were prepared by adding 5 ul of each

chemical standard into 1000 ul of methanol. Then, 3 liters of air was added to a tedlar bag (SKC, Eighty Four, PA). The appropriate volume of each test chemical was added to the tedlar bag to result in a final air concentration of 1 ppm for each chemical. After letting the chemical sit in the bag for 10 minutes, the bag was purged with a SKC personal sampling pump (SKC, Eighty Four, PA). The bag was purged three times to minimize losses to the wall of the bag. Upon the fourth filling, the bag was prepared to test the fibers.

Optimal Fiber Selection

Each type of fiber was exposed to a 1 ppm chemical mixture of the six test chemicals for 1 minute. The fiber was then inserted into the injection port of an Agilent 6850 gas chromatograph with a 5973 quadrapole mass selective detector (Agilent Technologies, Wilmington, DE) with the following instrumentation parameters:

GC Column: HP-5MS, 30m X 0.25 um ID X 0.25 um phase (Agilent Technologies, Wilmington, DE)
Carrier gas: Helium
Injection port temperature: 250 °C
Transfer line temperature: 180 °C
Oven ramping rate: initial temperature = 60 °C hold for 1 min, ramp at 20 °C/min to 180 °C and hold at 180 °C for 30 second
SPME Injection port liner: 0.75 mm ID deactivated glass (Supelco)

Triplicate samples of each fiber type were run and their peak areas were averaged. The fiber type with the greatest average TIC peak area for the chemical was selected as the optimal fiber for the chemical.

Determine SPME Sampling Time

Once the optimal fiber type was selected, an uptake curve was constructed for each of the six chemicals in order to determine an optimal sample extraction time for the

chemical. To meet the realistic need of an emergency scenario, the turn around time for a sample result needs to be within a reasonable time frame. For this study, extraction times of 20 sec, 40 sec, 1 min, 5 min, 10 min, 30 min, 45 min and 60 min were used. To collect data for the uptake curves, a standard mixture of 0.5 ppm of each chemical was prepared inside a 3 liter tedlar bag, following the procedure described under sample preparation, in the previous section. The selected fiber was exposed to the 0.5 ppm chemical mixture for the specified extraction times and then immediately analyzed in the HAPSITE SPME system.

Carryover Effect

The temperature of the HAPSITE SPME injection port was set at 270 °C to ensure complete desorption of the analytes from the fiber. Based on preliminary test data and to minimize carryover effect, a 2 minute desorption time was used. The desorption time is the length of time the fiber is left exposed in the injection port. At the end of the 2 minute desorption, the fiber was removed from the injection port and capped with a septum to ensure residual chemicals, if any, remained on the fiber. When the GC-MS run was completed, the same fiber was analyzed again to see if there was any residual chemical from the previous run remained in the fiber. In this study, carryover was considered to be present if any chemical in the mixture was detected in the fiber blank run with a SI above 400.

Data Analysis

In the optimal fiber selection process, the overall F-statistics from the one way analysis of variance (ANOVA) was used to determine whether the difference of the peak area was due to fiber coating type or by chance. If the F-statistical value was significant

(P value<0.05), the difference was due to the fiber coating type. Tukey's post hoc comparison method was used to confirm the source of the difference [31].

**Specific Aim 2:**

Estimate the lower limit of detection (LOD) and examine linearity across a range of concentrations of the six selected chemicals using the following sample introduction methods:

- Standard HAPSITE loop
- HAPSITE tri-bed concentrator
- HAPSITE SPME
- A field portable instrument with SPME

Compare the performance of HAPSITE sample introduction methods to a field portable instrument using SPME as the sample introduction method. The field portable instrument chosen for this comparison was the Viking model 573 GC/MS (Bruker Daltonics, Billerica, MA). The instrumentation parameters for the HAPSITE and the Viking were set as follows:

<u>HAPSITE</u>
GC Column: 2066-U Column (30 meter SPB-1) (30m X 0.32mm ID X 1 um 100% methyl silicon phase–Acrylate coated fused silica) .
Carrier gas: Nitrogen
Injection port temperature: 270° C
Transfer liner temperature: 60 °C
Oven ramping setting: 60 °C hold for 1min, ramp at 10 °C/min for 3 min, ramp at 20 °C/min for 4.5 min and hold at 180 °C for 2.5 min
SPME Injection port liner: No

<u>Viking model 573 (Bruker Daltonics, Billerica, MA).</u>
GC Column: 30 m X 0.25mm X 0.25 um DB5-MS EP-C240
Carrier gas: Hydrogen

Injection port temperature: 270 °C
Transfer liner temperature: 180 °C
Oven ramping setting: 60 °C hold for 1 min, ramp at 10 °C/min for 3 min, ramp at 20 °C/min for 4.5 min and hold at 180 °C for 2.5 min
SPME Injection port liner: 0.75 mm ID deactivated glass (Supelco)

A 1 minute SPME sample extraction time was used to remain consistent with the 1 minute standard HAPSITE Loop sampling method. Chemical mixtures of 0.002 ppm, 0.02 ppm, 0.2 ppm, 1 ppm, 2 ppm and 10 ppm were made following the sample preparation procedure described in specific aim 1. These samples were analyzed using the four different sample introduction methods. The HAPSITE tri-bed concentrator introduction method was only used for chemical concentrations that were not detected by the HAPSITE loop only method. Triplicate samples were collected at each concentration for each sample introduction method. In order to compare the chromatograms generated from both the Viking and HAPSITE, the Viking chromatograms were exported to NIST 2.0 MS search software (NIST library search). The forward search match factor for the Viking was compare to the HAPSITE SI number, because the HAPSITE SI number is equivalent to the NIST forward search match factor.

Data Analysis

To examine the linear range, the coefficient of determinant ($R^2$), was used to determine if there was any correlation between the sample concentrations and characteristic ion (the most abundant m/z in the spectrum) peak areas. For this experiment, the criterion for linearity was set at 0.95.

**Specific Aim 3:**

The quality of the HAPSITE loop, HAPSITE SPME and Viking SPME chromatography were compared. Peak width and peak symmetry were evaluated using chromatograms obtained in specific aim 2. Chemical concentrations of 1 and 10 ppm were used. When comparing the HAPSITE loop to the HAPSITE SPME, the GC and MS remained constant in the system. The variable in this comparison was the sample introduction method. Therefore, differences in the quality of the chromatography between the HAPSITE systems would primarily be limited to differences in the sample introduction method. This might be useful in identifying problems, such as active sites, dead space cold spots in the injection port.

**Specific Aim 4:**

Compare the reproducibility of the data obtained using the four different sample introduction methods listed in Specific Aim 2.

At each of the six concentrations, triplicate samples were obtained for all four sample introduction methods. The characteristic ions (see Table 3-1) of the six chemicals where obtained from extracted ion chromatograms and were used for this comparison. At each concentration, the RSD of the characteristic ion peak area was determined and used as a measure of reproducibility. A RSD below 25% was considered reproducible.

Table 3-1: Chemical's Characteristic Ions

| Chemical name | Characteristic Ion |
|---|---|
| Acrylonitrile | 53 |
| Benzene | 78 |
| Trichloromethane | 83 |
| 1,3,5-trimethylbenzene | 105 |
| o-chlorotoluene | 91 |
| Hexachlorobutadiene | 225 |

## CHAPTER FOUR: RESULTS AND DATA ANALYSIS

To select the chemicals used in this research, a distribution of molecular weights across the operating range (45 to 300 AMU) of the HAPSITE were used as the selection criteria. Also, the chemicals boiling point had to be less than 572° F, which is the upper limit for the HAPSITE instrument. Given these criteria, the chemicals listed in Table 4-1 were chosen for this study.

**Table 4-1:** Chemical Properties for Six Test Chemicals

| Chemical | Molecular Weight (AMU) | Boiling Point (° F) |
|---|---|---|
| Acrylonitrile | 53 | 171 |
| Benzene | 78 | 176 |
| Trichloromethane | 119 | 143 |
| 1,3,5-trimethylbenzene | 120 | 329 |
| o-chlorotoluene | 126 | 323 |
| Hexachlorobutadiene | 260 | 419 |

SPME Fiber Selection

To select the SPME fiber used in this research, three fiber types were exposed to a 1 ppm mixture for an extraction time of 1 minute and then analyzed on a Viking 573 GC/MS (Bruker Daltonics, Billerica, MA). Of the three fibers, PDMS, PDMS/DVB and PA, the PDMS/DVB had the highest peak area (best sensitivity) for all six chemicals (Appendix A). Under these conditions, both the PA and PDMS fibers were able to detect only two out of the six chemicals.

Figures 4-1 and 4-2 illustrate the uptake curves for the six chemicals using the PDMS/DVB fiber. Typically, the uptake curve will rise as extraction time increases as shown in Figure 4-1. Figure 4-2 shows very different uptake curves for benzene,

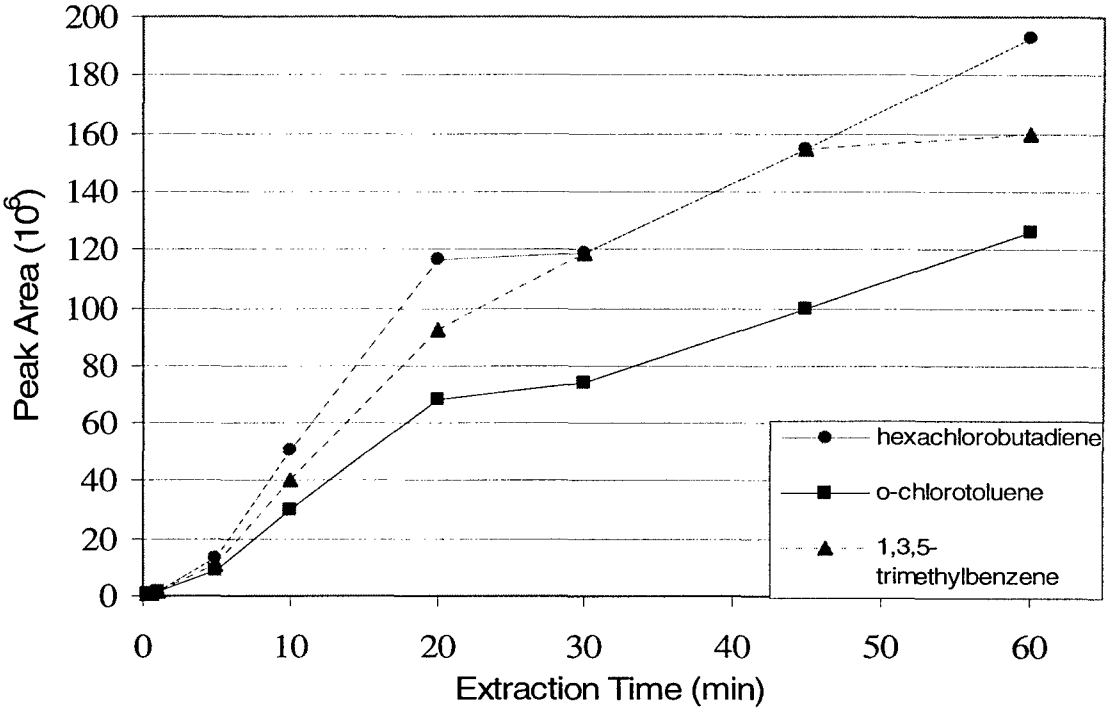



**Figure 4-1**: Extraction time versus chemical uptake (PDMS/DVB in 500 ppb chemical mixture)

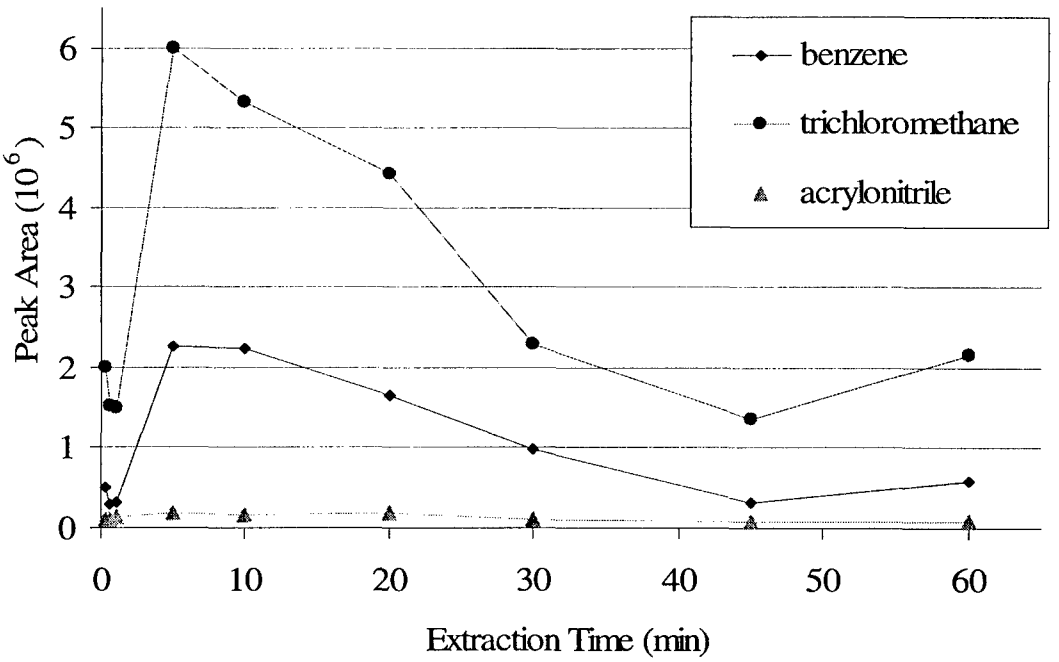



**Figure 4-2:** Uptake curves for benzene, trichloromethane and acrylonitrile (PDMS/DVB fiber in 500 ppb benzene)

trichloromethane and acrylonitrile. Instead of rising and reaching a plateau, the curves reach a maximum peak and then begin to decrease as the extraction time increases. The decrease in peak area for these chemicals is likely the result of competitive displacement. Unlike PDMS and PA fibers that extract analytes via a non-competitive absorption process, PDMS/DVB extracts analytes via adsorption. Adsorption is a competitive uptake mechanism, where the chemicals compete for a limited number of active sites on the fiber surface [12].

To test the theory that the decrease observed in Figure 4-2 is due to competitive displacement, the peak areas for dimethylacetamide and phenol (known impurities from a tedlar bag), were plotted along with the benzene peak area in Figure 4-3. These same relationships exist for the trichloromethane and the acrylonitrile samples as well.

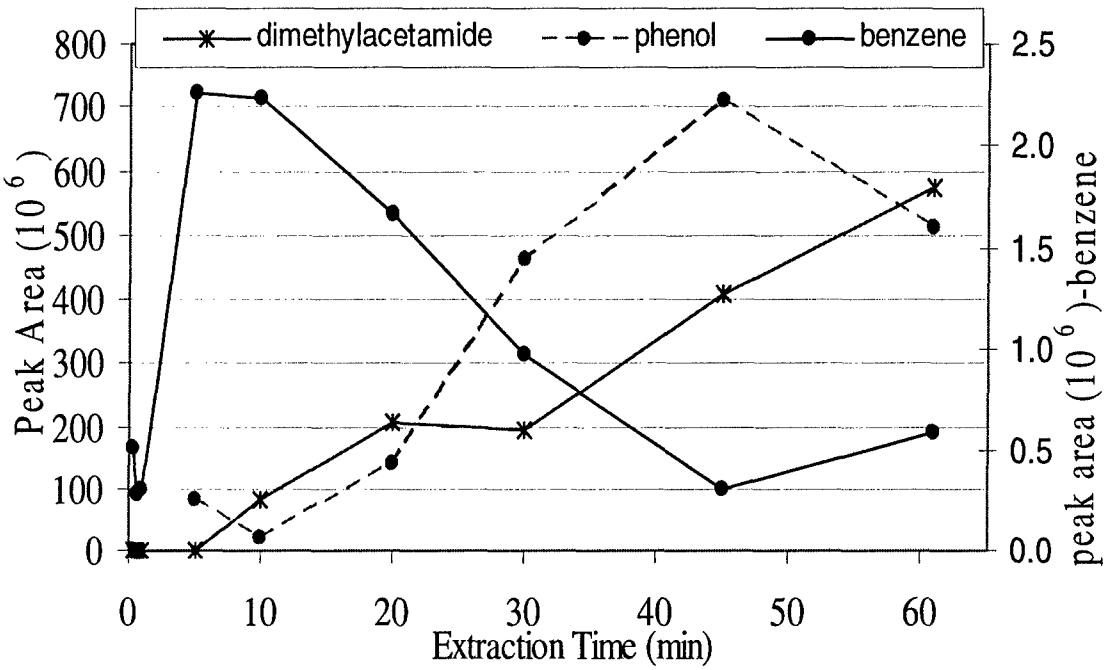



**Figure 4-3:** Uptake Curves for Benzene and Tedlar Bag Impurities (PDMS/DVB fiber in 500 ppb benzene)

This suggests the increase in the phenol and dimethylacetamide onto the PDMS/DVB fiber caused the decrease in the benzene peak area. The impurities were preferentially extracted by the PDMS/DVB coating and thus eventually displaced the analytes of interest. Because of the complication with competitive displacement, the PDMS fiber, which is not subject to competitive displacement, was selected for the rest of this research despite the fact that PDMS was not as sensitive as the PDMS/DVB fiber.

Of the six chemicals tested, there was minor carryover for three chemicals: trichloromethane, 1,3,5-trimethylbenzene and hexachlorobutadiene. However, the carryover was minimal. The largest amount of carryover was observed for trichloromethane, which demonstrated carryover in the blank sample of only 0.05% of the peak observed in the previous sample run.

**Limit of Detection**

The SI for all four sampling methods for the six chemicals at six concentrations are illustrated in Table 4-2. A chemical was considered detectable if the SI was above 700. The table provides the average of the triplicate samples. The first two data columns are a comparison between the SPME fiber used with the Viking GC/MS against the HAPSITE GC/MS. The third data column is the SI value for the HAPSITE minus the Viking SI value. The column labeled "HAPSITE Loop" and the column labeled "HAPSITE Concentrator" describes sample introduction using the sampling probe alone and the probe with a tri-bed concentrator.

In general, a comparison between the SI of the HAPSITE SPME and the Viking SPME indicates there is a better match (higher SI) when using the HAPSITE SPME as

**Table 4-2**: Summary of SI for the Four Different Sample Introduction Methods

| | Conc (ppm) | HAPSITE SPME | Viking SPME | HAP-Vik SPME | HAPSITE Loop | HAPSITE Concentrator |
|---|---|---|---|---|---|---|
| Acrylonitrile MW = 53 | 0.002 | | | | | |
| | 0.02 | | | | | |
| | 0.2 | | | | | 915 |
| | 1 | 982 | | | 756 | |
| | 2 | 755 | 379 | 376 | 925 | |
| | 10 | 789 | 432 | 357 | 878 | |
| Benzene MW = 78 | 0.002 | | | | | 829 |
| | 0.02 | 496 | 343 | 153 | | 653 |
| | 0.2 | 409 | 398 | 11 | | 952 |
| | 1 | 702 | 586 | 116 | 759 | |
| | 2 | 811 | 799 | 12 | 785 | |
| | 10 | 915 | 930 | -15 | 898 | |
| Trichloromethane MW = 119 | 0.002 | | | | | 847 |
| | 0.02 | | | | | 706 |
| | 0.2 | | 364 | | | 927 |
| | 1 | 685 | 550 | 135 | 714 | |
| | 2 | 822 | 770 | 52 | 851 | |
| | 10 | 773 | 906 | -133 | 912 | |
| 1,3,5-Trimethylbenzene MW=120 | 0.002 | | | | | |
| | 0.02 | 660 | 538 | 122 | | 677 |
| | 0.2 | 688 | 854 | -166 | | 887 |
| | 1 | 894 | 940 | -46 | 765 | |
| | 2 | 898 | 932 | -34 | 808 | |
| | 10 | 924 | 938 | -14 | 894 | |
| o-Chlorotoluene MW = 126 | 0.002 | | | | | 516 |
| | 0.02 | | 420 | | | 790 |
| | 0.2 | 755 | 804 | -49 | | 921 |
| | 1 | 880 | 899 | -19 | 725 | |
| | 2 | 910 | 910 | 0 | 650 | |
| | 10 | 927 | 918 | 9 | 862 | |
| Hexachlorobutadiene MW=260 | 0.002 | | | | | 586 |
| | 0.02 | 610 | 646 | | | 779 |
| | 0.2 | 815 | 931 | -116 | | 835 |
| | 1 | 893 | 910 | -17 | 652 | |
| | 2 | 907 | 778 | 129 | 772 | |
| | 10 | 887 | 936 | -49 | 854 | |

Darkened areas under the HAPSITE Tri-bed concentrator column signify that samples were not accomplished. Hashed areas indicate the analyte was not detected (SI < 400), numbers with shading indicate SI < 700.

opposed to the Viking SPME for the two lowest MW chemicals. The four chemicals with a higher MW are more mixed between the Viking and the HAPSITE showing about the same degree of ability to match the chemical to the NIST library. Note also that the SPME methods were not able to match the chemical at the lowest concentration. The best matching for the SPME methods (SI > 700) only starts to occur when the chemical concentrations exceeded 1 ppm.

The HAPSITE Loop and HAPSITE concentrator columns in Table 4-2 also show an interesting breakpoint near 1 ppm concentrations. Recall that the experiment started at the highest concentration with the HAPSITE Loop method and the concentrations were reduced until the SI dropped below 700. When the HAPSITE Loop had an SI < 700, the tri-bed concentrator was installed. The ability of the HAPSITE to detect at the lowest concentrations were improved with the concentrator. In fact, the concentrator method was the only configuration that was able to detect at the lowest concentrations. This makes sense in that the tri-bed concentrator, like any solid phase concentrating material, is designed to collect a larger fraction of the chemicals for introduction into the GC/MS resulting in better chemical identification.

The LOD can be estimated using Table 4-2. If the SI for a given concentration was below 700, then the LOD was assumed to be between that concentration and the concentration at which the SI was above 700. For example, the HAPSITE SPME LOD for benzene was estimated to be between 0.2 ppm (SI = 409) and 1 ppm (SI = 702). Table 4-3 is a summary of the LODs assumed using these criteria. The LOD for the Viking and the HAPSITE SPME are similar except the two chemicals with the lowest MW where the

**Table 4-3**: Summary Range of LOD (ppm)

| | Sample Introduction Method | | | |
|---|---|---|---|---|
| **Chemical** | **HAPSITE SPME** | **Viking SPME** | **HAPSITE Loop** | **HAPSITE Tri-bed Concentrator** |
| Acrylonitrile MW = 53 | 0.2 - 1 | | 0.2 - 1 | 0.02 - 0.2 |
| Benzene MW = 78 | 0.02 - 0.2 | | 0.2 - 1 | < 0.002 |
| Trichloromethane MW = 119 | | | 0.2 - 1 | < 0.002 |
| 1,3,5-Trimethylbenzene MW=120 | 0.02 - 0.2 | 0.02 - 0.2 | 0.2 - 1 | 0.002 - 0.02 |
| o-Chlorotoluene MW = 126 | 0.02 - 0.2 | 0.02 - 0.2 | 0.2 - 1 | 0.02 - 0.2 |
| Hexachlorobutadiene MW=260 | 0.02 - 0.2 | 0.02 - 0.2 | 1 - 2 | 0.002 - 0.02 |

HAPSITE SPME had a lower LOD. As expected, the LOD is lowest for the HAPSITE Tri-bed concentrator.

## Linearity

The R squared ($R^2$) value for each method was used to measure linearity for all six chemicals. Only concentrations with an SI > 400 were used to compute the $R^2$. The linearity is a measure of the peak area against the test concentration. Figure 4-4 illustrates the triplicate samples for benzene for the HAPSITE SPME method along with the $R^2$ value. The $R^2$ values for all methods are shown in Table 4-4. The $R^2$ for all methods exceeded 97% except the HAPSITE Tri-bed concentrator method which are shaded in Table 4-4. This is partly due to the fact that the concentrations were so low for the HAPSITE Tri-bed concentrator method. When concentrations become very low, variability tends to increase which impacts linearity.

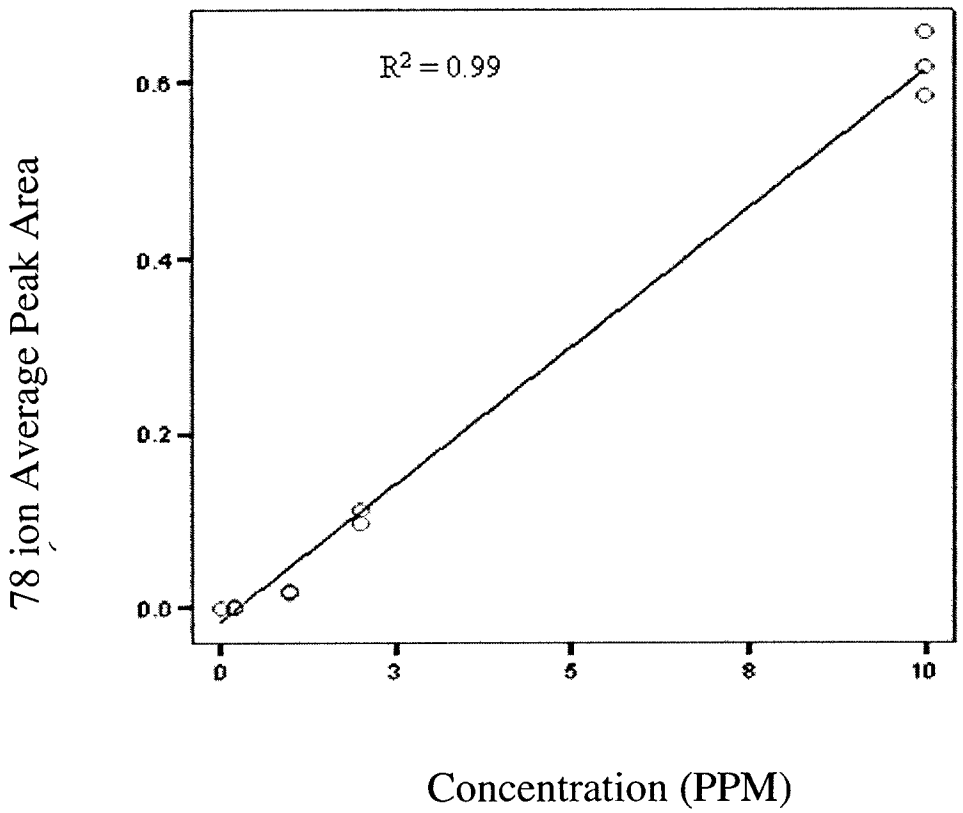



**Figure 4-4**: HAPSITE SPME calibration curve for benzene using the 78 characteristic ion with PDMS fiber and 1 minute extraction time

**Table 4-4**: Summary of $R^2$ in Percent

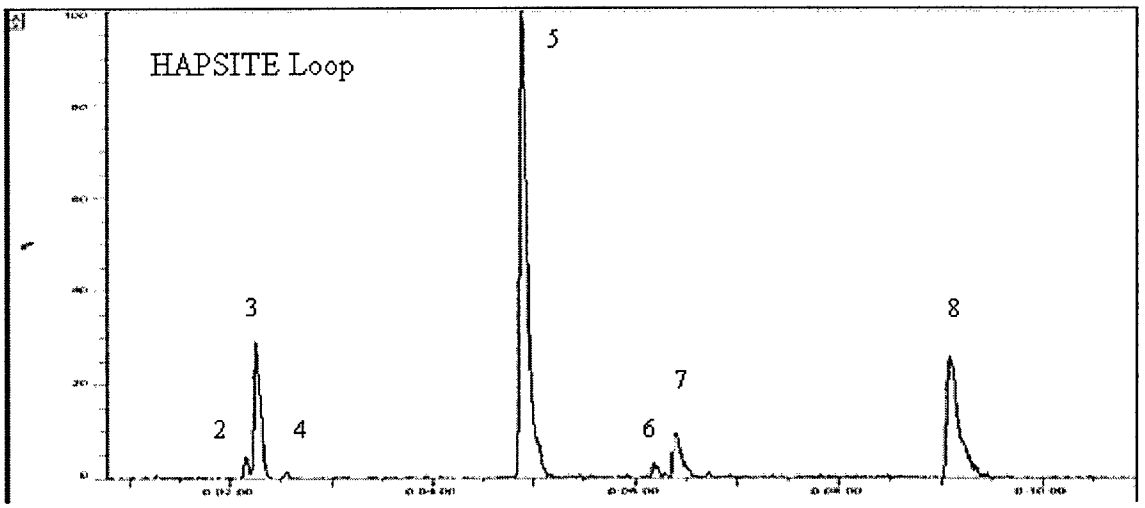
| | Sample Introduction Method | | | |
|---|---|---|---|---|
| **Chemical** | **HAPSITE SPME** | **Viking SPME** | **HAPSITE Loop** | **HAPSITE Tri-bed concentrator** |
| Acrylonitrile MW = 53 | 95% | 97% | 98% | 99% |
| Benzene MW = 78 | 99% | 99% | 98% | 33% |
| Trichloromethane MW = 119 | 99% | 99% | 97% | 75% |
| 1,3,5-Trimethylbenzene MW=120 | 99% | 100% | 99% | 98% |
| o-Chlorotoluene MW = 126 | 99% | 100% | 100% | 91% |
| Hexachlorobutadiene MW=260 | 100% | 97% | 96% | 99% |

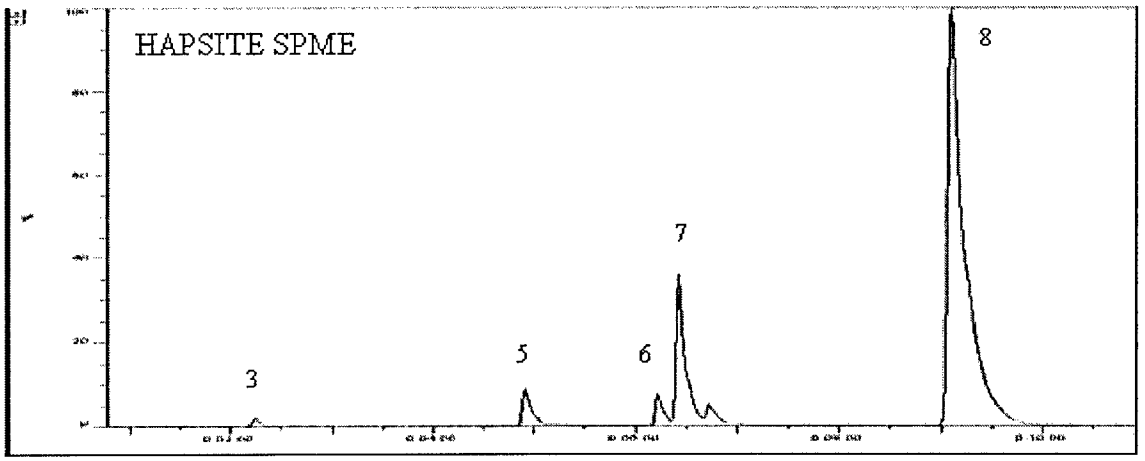
Shading is R2 below 95%

**Quality of Chromatography**

Specific Aim 3 was to compare the quality of the chromatography. Figure 4-5 and 4-6 are used to illustrate some differences at 1 ppm and 10 ppm concentrations. In both figures, three chromatograms are displayed: HAPSITE Loop, HAPSITE SPME and the Viking SPME methods. All three chromatographs are aligned by the retention time (x-axis). Note that the same chemicals have shorter retention times on the Viking chromatograph than the HAPSITE chromatographs due to differences in carrier gas velocity. In Figure 4-5 (1 ppm), the HAPSITE Loop method shows the chemical with the highest peak area was the HAPSITE internal standard (BPFB) (Point 5). For HAPSITE SPME chromatogram and Viking SPME chromatogram, the Hexachlorobutadiene (Point 8) had the highest relative abundance rather than the internal standard (Point 5). This demonstrates the concentrating benefit of SPME sampling. Furthermore, the extraction selectivity of SPME sampling is demonstrated by the preferential extraction of hexachlorobutadiene over the other chemicals in the mixture.

In both Figures 4-5 and 4-6, there is more tailing in both of the HAPSITE chromatograms versus the Viking SPME method. Peaks for all chromatogram are relatively symmetrical, except the hexachlorobutadiene peaks in the HAPSITE chromatograms. The peak base widths as well as peak resolution of the HAPSITE Loop and HAPSITE SPME for both in Figures 4-5 and 4-6 are very similar. Peak base widths for the Viking methods have much narrower widths than those of the HAPSITE methods. This is due to inherent design features. For example, the HAPSITE uses a nitrogen carrier gas, has a polymeric MS interface membrane, has a lower transfer line temperature whereas the Viking uses hydrogen carrier gas, does not have a polymeric MS interface



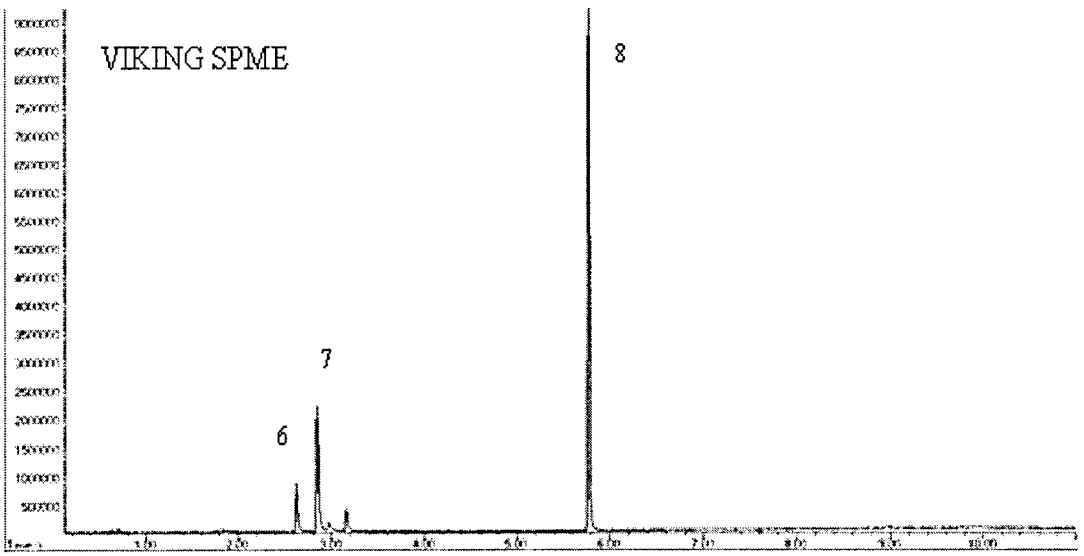




**Figure 4-5:** A Six 1 ppm chemical mixture, 1 minute loop fill, with PDMS fiber.
1: Acrylonitrile,2: Trichloromethane, 3: Internal standard #1 (TRIS), 4: Benzene, 5: Internal standard #2 (BPFB), 6: o-chlorotoluene, 7: 1,3,5-trimethylbenzene, 8: hexachlorobutadiene

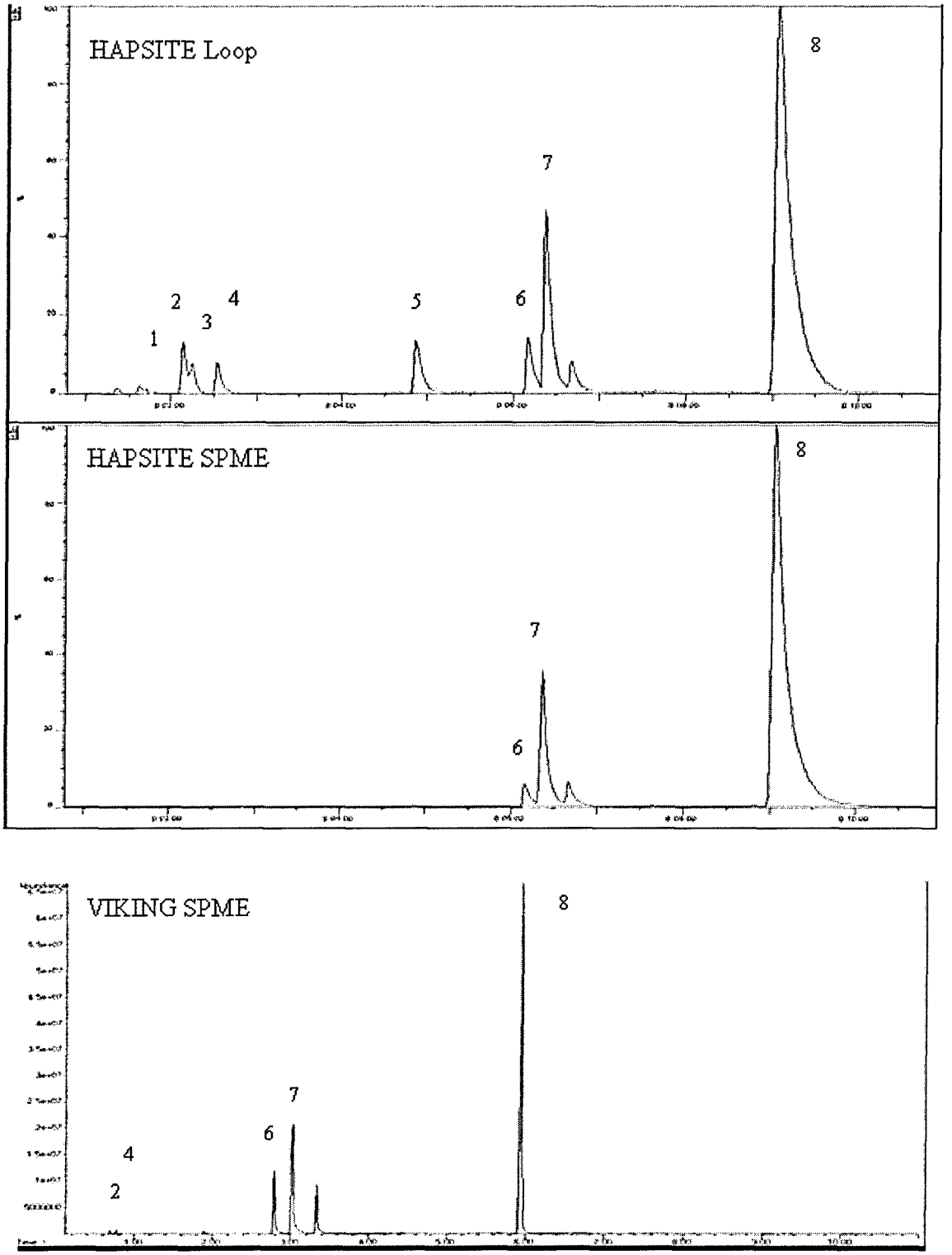



**Figure 4-6**: A six 10 ppm chemical mixture, 1 minute loop fill with PDMS fiber.
1: Acrylonitrile,2: Trichloromethane, 3: Internal standard #1 (TRIS), 4: Benzene, 5: Internal standard #2 (BPFB), 6: o-chlorotoluene, 7: 1,3,5-trimethylbenzene, 8: hexachlorobutadiene

membrane and has a higher transfer line temperature. Overall, the peaks in Viking chromatograms have better peak resolution than the peaks in the HAPSITE chromatograms.

**Reproducibility**

Specific Aim 4 was to test the reproducibility of the four methods. The value of the RSD is an indication of the reproducibility of the sample. Table 4-5 is a summary of peak area RSDs for all methods. For the four chemicals wit the highest MW, the HAPSITE SPME and the Viking SPME have RSD values below approximately 25% from concentration of 1 ppm concentrations and above. The RSDs between the HAPSITE SPME and the Viking SPME are similar, and the RSDs tend to get smaller as the MW of the chemicals increase. The RSDs of the HAPSITE Loop are, in most cases, higher than RSDs for both the SPME methods. In addition, an RSD could not even be established at some of the concentrations that an RSD was established with the SPME methods. This is probably due to the fact that SPME concentrates analytes and therefore can detect at a lower concentration than HAPSITE loop. If the instrument could not detect the analyte on at least two runs at a given concentration, the RSD could not be calculated. Overall, the HAPSITE SPME was as reproducible as the Viking SPME method and the SPME methods appear to have better reproducibility than the HAPSITE Loop method.

During the study, there were a few incidences when the "column pressure error" appeared within the first two minutes of the sample run when the SPME introduction method was used. The HAPSITE stopped running when the message appeared. This might be caused by a pressure leak around the SPME injection port. It is possible that the opening of the ball seat was not sealed tightly by the high precision ball as shown in

**Table 4-5:** Characteristic ion peak area RSDs (%) Summary

| | Conc ppm | HAPSITE SPME | VIKING SPME | HAP-Vik SPME | HAPSITE LOOP | HAPSITE Concentrator |
|---|---|---|---|---|---|---|
| Acrylonitrile MW = 53 | 0.002 | | | | | |
| | 0.02 | | | | | 82.38 |
| | 0.2 | | | | | 4.67 |
| | 1 | | | | 61.07 | |
| | 2 | 84.43 | | | 10.10 | |
| | 10 | 22.58 | 4.79 | 17.79 | 12.66 | |
| Benzene MW = 78 | 0.002 | | | | | 28.78 |
| | 0.02 | | | | | 35.08 |
| | 0.2 | | | | | 12.70 |
| | 1 | 20.40 | 25.68 | -5.28 | 60.05 | |
| | 2 | 8.50 | 18.14 | -9.63 | 3.46 | |
| | 10 | 5.85 | 5.81 | 0.03 | 14.43 | |
| Trichloromethane MW = 119 | 0.002 | | | | | 29.43 |
| | 0.02 | | | | | 70.15 |
| | 0.2 | | | | | 9.84 |
| | 1 | 13.22 | | | 67.17 | |
| | 2 | 8.87 | 15.36 | -6.49 | 3.47 | |
| | 10 | 9.10 | 5.78 | 3.32 | 15.95 | |
| 1,3,5-Trimethylbenzene MW=120 | 0.002 | | | | | 5.30 |
| | 0.02 | | | | | 42.13 |
| | 0.2 | 7.24 | 21.78 | -14.53 | | 4.74 |
| | 1 | 7.98 | 2.77 | 5.21 | 29.99 | |
| | 2 | 1.16 | 2.44 | -1.28 | 7.90 | |
| | 10 | 7.57 | 0.83 | 6.74 | 3.71 | |
| o-Chlorotoluene MW = 126 | 0.002 | | | | | 9.04 |
| | 0.02 | | | | | 11.82 |
| | 0.2 | 10.75 | 16.23 | -5.49 | | 13.13 |
| | 1 | 4.81 | 7.43 | -2.63 | 62.60 | |
| | 2 | 2.28 | 6.02 | -3.74 | 4.57 | |
| | 10 | 9.69 | 1.91 | 7.78 | 8.36 | |
| Hexachlorobutadiene MW=260 | 0.002 | | | | | 15.46 |
| | 0.02 | 13.98 | 10.30 | 3.68 | | 7.92 |
| | 0.2 | 2.89 | 12.75 | -9.87 | | 11.02 |
| | 1 | 9.17 | 4.02 | 5.15 | 30.94 | |
| | 2 | 0.47 | 1.96 | -1.50 | 40.32 | |
| | 10 | 1.19 | 17.59 | -16.41 | 17.04 | |

Darkened areas under the HAPSITE Tri-bed concentrator column signify that samples were not accomplished. Hashed areas means the analyte was not detected or only one of the triplicate samples was detected, numbers with shading indicate RSD > 25

Figure 1-2. The problem only occurred a few times when the SPME fiber was quickly extracted. When the fiber was extracted more slowly, the problem did not occur. This may be a consideration if this type of injection port is used in other HAPSITE instruments.

# CHAPTER FIVE: CONCLUSIONS

With the HAPSITE SPME system, responders can collect samples using a small and light weight SPME fiber, making sample collection much easier than taking the entire HAPSITE unit into the hot zone and collecting samples with the HAPSITE probe. The HAPSITE SPME system was shown to provide reliable and reproducible sample results for concentrations above 1 ppm. Both the SI and LOD generated from the HAPSITE were comparable to those generated from the Viking SPME system. Among the four sample introduction methods used in this research, Viking SPME provided chromatograms with the best quality. The chromatogram had better peak resolution and narrower peak widths than the other three sample introduction methods. In addition, the HAPSITE Tribed Concentrator sample introduction method detected chemicals at a much lower concentration than the other systems.

## Study Limitations

A limitation of this study is its inability to generalize the results to the chemicals that could be encountered in a field environment. Since only six chemicals were selected and tested, how these chemicals behave may not be representative of the entire range of chemicals in the operation range of the HAPSITE.

A second limitation may result from potential interaction when chemical standards were combined. Interactions between chemicals may occur. The interaction might alter the response of chemicals during the sampling or analytical process. However, this is believed to represent a realistic condition in the environment where sampling and analysis of an atmosphere containing only a single pure chemical is unlikely. Since tedlar bags were used for this study, impurities such as phenol,

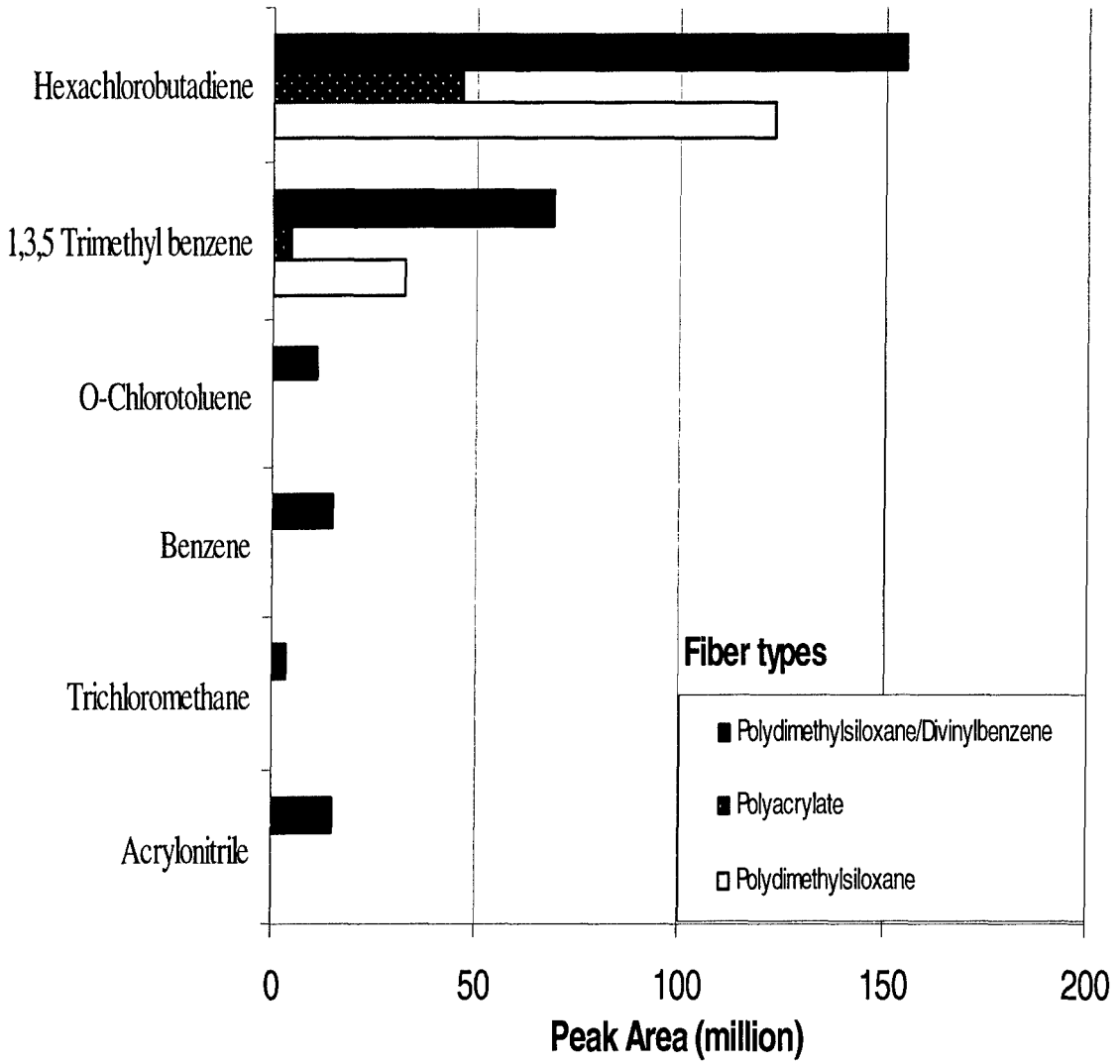
dimethylacetamide, associated with tedlar bags were found in samples. The presence of these impurities affected the uptake kinetic of the chemicals that were tested when fiber with adsorption as the extraction mechanism, such as PDMS/DVB was used. Although PDMS/DVB was found to be the optimal fiber, the PDMS fiber was used for the latter part of the study so that competitive displacement would not become an issue.

A third limitation may be insufficient data points. The six selected chemicals were run at chemical concentrations 0.002, 0.02, 0.2, 1, 2 and 10 ppm. There was no data between 2 ppm and 10 ppm. More tests should be run in this range in order to confirm whether the chemical is linear across the 0.002 – 10 ppm range.

Finally, this study was performed in a laboratory, not in the harsh conditions for which the HAPSITE would likely be used. The prototype HAPSITE SPME injection port was powered from an external power supply and therefore the power supply was not an issue in this study. However, if the prototype were to be deployed in the field and the standard battery was used as the source to power, the operation of HAPSITE SPME system, the life of the battery would be shortened.

## APPENDIX A

Peak area of six chemicals tested for all three fiber types (in a 1ppm mixture for an extraction time of 1 minute)



## Appendix B

Peak Area ($10^6$) for 500 ppb mixture, using a PDMS fiber 1 minute extraction time

| | Conc ppm | HAPSITE SPME | VIKING SPME | HAP-Vik SPME | | HAPSITE LOOP | HAPSITE Concentrator |
|---|---|---|---|---|---|---|---|
| Acrylonitrile MW = 53 | 0.002 | | | | | | |
| | 0.02 | | | | | | |
| | 0.2 | 0 | | | | | 3.517 |
| | 1 | 0.001 | 0 | 0.001 | | 0.001 | |
| | 2 | 0.003 | 0.003 | 0 | | 0.016 | |
| | 10 | 0.011 | 0.015 | -0.004 | | 0.088 | |
| Benzene MW = 78 | 0.002 | | | | | | 0.131 |
| | 0.02 | 0.004 | 0 | 0.004 | | | 17.956 |
| | 0.2 | 0.014 | 0.001 | 0.013 | | | 18.938 |
| | 1 | 0.047 | 0.018 | 0.029 | | 0.004 | |
| | 2 | 0.115 | 0.123 | -0.008 | | 0.089 | |
| | 10 | 0.426 | 0.619 | -0.193 | | 0.571 | |
| Trichloromethane MW = 119 | 0.002 | | | | | | 0.104 |
| | 0.02 | | 0.001 | | | | 6.514 |
| | 0.2 | 0.005 | 0.001 | 0.004 | | | 14.409 |
| | 1 | 0.025 | 0.018 | 0.007 | | 0.015 | |
| | 2 | 0.077 | 0.102 | -0.025 | | 0.12 | |
| | 10 | 0.275 | 0.417 | -0.142 | | 0.645 | |
| 1,3,5-Trimethylbenzene MW=120 | 0.002 | | | | | | 0.588 |
| | 0.02 | 0.025 | 0.031 | -0.006 | | | 4.669 |
| | 0.2 | 0.281 | 0.522 | -0.241 | | | 13.267 |
| | 1 | 1.388 | 5.4 | -4.012 | | 0.083 | 4.669 |
| | 2 | 2.946 | 20.307 | -17.361 | | 0.279 | |
| | 10 | 14.606 | 101.914 | -87.308 | | 2.164 | |
| o-Chlorotoluene MW = 126 | 0.002 | | | | | | 0.105 |
| | 0.02 | 0.011 | 0.002 | 0.009 | | | 2.984 |
| | 0.2 | 0.139 | 0.133 | 0.006 | | | 23.541 |
| | 1 | 0.593 | 1.08 | -0.487 | | 0.018 | |
| | 2 | 1.416 | 4.019 | -2.603 | | 0.086 | |
| | 10 | 6.589 | 19.046 | -12.457 | | 0.641 | |
| Hexachlorobutadiene MW=260 | 0.002 | | | | | | 0.032 |
| | 0.02 | 0.006 | 0.059 | -0.053 | | | 3.829 |
| | 0.2 | 0.217 | 0.935 | -0.718 | | | 38.213 |
| | 1 | 1.007 | 7.98 | -6.973 | | 0.041 | |
| | 2 | 1.568 | 20.94 | -19.372 | | 0.082 | |
| | 10 | 8.282 | 114.341 | -106.059 | | 0.986 | |

Darkened areas under the HAPSITE Tri-bed concentrator column signify that samples were not accomplished. Hashed areas means the analyte was not detected

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